Supplemental Information:

Fertilizer derived from alkaline hydrothermal alteration of K-feldspar: a micrometer to nanometer-scale investigation of K in secondary reaction products and the feldspar interface

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Supplemental information 1

The extraction of potassium from natural sources has a long history, going back to Antiquity. As detailed in an historical perspective by Ciceri et al. (2015), potassium has been extracted since the 18th century from a variety of natural sources, including wood ash, kelp, and barilla- which is obtained by burning salt tolerant (halophyte) plants. Starting from the second half of the 19th century the direct mining and application of soluble potassium salts (e.g., sylvite- KCl, saltpeter- KNO₃, potash sulfate- K₂SO₄, potash- K₂CO₃, and others) as a K-fertilizer took off, and has since that time dominated the international market. The interested reader should refer to Table 1 in Ciceri et al. (2015) for a complete list of various processes (heat treatment, aqueous alteration) that have been developed over the past century to extract potash from K-bearing feldspar.

Supplemental information 2

Preliminary small-scale agronomy tests using hydrothermally altered K-feldspar have been carried out and reported in the literature. For example, Ciceri et al. (2019) report that tomato plants treated with either KCl or hydrothermal product were healthier due to uptake of K, compared to treatment with unaltered K-feldspar. Nonetheless, the very slow release of K from just unaltered K-feldspar does, in some cases, also procure beneficial effects on crop growth (Sanz Scovino and Rowell, 1988).

Fertilizer from hydrothermally processed K-feldspar also contains other phases and elements that are potentially important for remediating nutrient poor soils. Tropical soils, which are characteristically K-poor, are also generally acidic, and thus the addition of calcium carbonate is ideally suited for its acid neutralization properties. Moreover, addition of calcium ions to soils is beneficial for reducing Al concentrations, increasing P availability, promotion of N₂ fixation in legumes (O'Hara et al., 1988), and fortifying growth of new plant tissue. Many of the hydrothermal product phases are silicate minerals, and fortuitously it turns out that silicon release to soils has also been proven to have beneficial effects. Thus, the high silica content of the hydrothermal product can be considered to be an important potential fertilizer property. Silicon is known to increase crop yields, promote upright growth and pathogen resistance, and mitigate the effects of abiotic stress, such as drought, and the presence of heavy metals and aluminum in soils (Guntzer et al., 2012; Cuong et al., 2017).

It is even possible to envision the use of hydrothermally altered K-feldspar for broader applications, such as soil contaminant remediation. A few studies have shown that K-feldspar-derived hydrothermal alteration products can contain Al-substituted tobermorite (Yang et al., 2015; Ciceri et al., 2017), which is attributed to combined Al³⁺ + Na⁺ substitution for Si⁴⁺. Al-substituted tobermorite can, in fact, be synthesized via a variety of hydrothermal chemical processes (e.g., Reinik et al., 2007; Mostafa et al.,

2009). Experimental evidence reveals that this phase possesses reversible cation exchange properties, useful for radioactive and hazardous cation separation (Youssef et al., 2010; Wang et al., 2017). In particular, synthetic Al-substituted tobermorite has a particular affinity for the selective uptake of Cs (Komarmeni et al., 1987). Thus, K-feldspar hydrothermal product containing Al-substituted tobermorite could serve as a dual-purpose material, satisfying a need as both a K-fertilizer and a remediation agent in soils.

Supplemental Information 3

There are many well-known limitations of SEM-EDX measurements that apply to our study. One of the main ones is related to the electron interaction volume, whose geometry is roughly pear-shaped. At depth the interaction volume is significantly wider than the spot size of the electron beam that impinges upon the surface of the sample. Secondary electrons, backscattered electrons, and characteristic X-rays originate from different depths of the interaction volume. The interaction volume and electron trajectories at depth can be calculated and visualized via Monte Carlo electron simulations. The depth and dimensions of the electron interaction volume, which depend on factors such as the accelerating voltage (energy of electrons) and density/composition of the sample, are by far larger than the 3-D dimensions of the individual particles that comprise the amalgams of intergrown and overlapping secondary precipitates. Therefore, the FESEM-EDX chemical measurements that we obtained do not represent the chemical compositions of individual secondary phases. Only the measured chemical composition of truly precipitate-free feldspar surfaces can be considered to be representative of a single phase.

The EDX spectra that were collected allowed us to determine the background subtracted and ZAF-corrected concentrations of K, Na, Ca, Al, Si, O and C at each spot analysis. Spot chemical analyses of sanidine and microcline grains devoid of surface precipitates are in good accord with XRF measurements of the unaltered grains (Table 1a, main text). This demonstrates that the spot analyses can be considered to be at least semi-quantitative. We also measured the chemistry of an aragonite seashell, and the results are also in accord with the nominal stoichiometry of this calcium carbonate polymorph (EDXS yielded the following composition in atom %: Ca = 18.4; C = 21.1; O = 60.5). Unfortunately, we were not able to obtain pure standards of the CASH and CSH minerals observed in this study for the purpose of EDXS analyses. However, these phases did not occur in homogeneous and pure crystalline masses in the secondary product. Only in rare cases could we observe and measure the chemistry of crystal aggregates that appeared to be composed of a single homogeneous phase (e.g. calcite). In the majority of cases, the precipitates within an analyzed spot were an amalgam of several crystalline phases with crystal sizes much smaller than the spot size. In these cases, the limitations of SEM-EDXS analyses discussed immediately above must be kept in mind. In addition, interpretation of measured C concentrations requires attention due to the ubiquitous nature of the C-based resin that was present in the interstitial spaces of the hydrothermal product.

Supplemental Information 4

The ‘smart phase mapping’ software measures and compares the EDX spectrum of 3 x 3 pixel blocks of a specified area. Pixel blocks with the same spectral range are given the same color and are assigned a certain ‘chemical phase’, and if the next pixel block is different, it is assigned to a new phase and color. The comparison is based on an internal tolerance value of spectral differences. Then, using an internal algorithm, the software automatically generates a multi-colored phase map, with the partitioning of phases indicated in a dynamic pie chart. The phase percentages (pie chart and chemical phase map) are based on the areal extent of each phase (i.e. pixel blocks). Specific chemical compositions belonging to a certain color on a map may correspond to a precise thermodynamic phase, such as might be the case for distinct minerals in a petrographical thin section. Alternatively, a phase may simply correspond to a certain relative chemical composition. In our case, the latter definition is applicable, with the exception of non-altered microcline and sanidine grain surfaces having no surface veneer of secondary precipitates. Thus, in this study we use the term ‘chemical phases’ when discussing phase maps. On a more quantitative level, the distribution of elements making up each phase is based on a weighted average of EDXS measurements.

In addition to the caveats mentioned directly above, because the authigenic precipitates in our samples are a dense amalgam of intergrown and overlapping phases with nm to μm -scale dimensions, the phases defined by specific compositions do not correspond to the exact chemical compositions of the secondary phases we measured by XRD and Rietveld refinement. Furthermore, the number of phases generated by the software was variable during our analyses, resulting in some maps with a dozen phases, and in other cases, only half as many, or even less. Such factors as elemental concentrations, counting time, background height, topography, etc. all have the ability to influence phase mapping results.

Supplemental Information 5

As opposed to spot analyses (FESEM-EDXS), scanning TEM-EDXS chemical analyses were based on small rectangular areas, from a few tens of nm to a maximum of 200 nm on a side. The obvious advantage of (S)TEM is the ability to choose areas for imaging and analysis at much higher magnification. All (S)TEM observations and measurements were done on samples prepared by FIB (see 2.6, main text). Focused ion beam-prepared ultrathin lamellae afforded us the possibility of selecting suitable interfacial areas on cross sectional slices that show primary K-feldspar grains and their surrounding coronas of secondary authigenic phases.

There is another important fundamental difference in the analytical measurements by FESEM-EDXS compared to (S)TEM-EDXS- the information depth is significantly shallower with respect to the latter technique. Because FIB foils are thin, the information depth for each STEM-EDXS analysis can be considered to be equal to the thickness of the FIB foil. In this study, we estimate this to be roughly 150-

200 nm, which corresponds to the thickness range of an average lamella. The intergrown nature and small dimensions of the secondary precipitates precluded obtaining the chemical composition of individual phases. This holds true for nearly all STEM-EDXS measurements in this study, even though the interaction volume and the information depth and volume are orders of magnitude less compared to (FE)SEM-EDX.

The entire set of STEM-EDXS analyses is reported in Table 4 (main text), and are reported as (relative) atom % concentrations of just 4 elements: Al, Si, K, and Ca. It is therefore important not to confuse these relative concentrations with the complete elemental compositions measured by FESEM-EDXS and reported in Table S2. In general, STEM-EDX measurements of Si, Al, O, K, Ca, Na and C should be considered with precaution. We have assumed that the ‘thin-film’ criterion holds (Cliff and Lorimer, 1975), which is based on the approximation that X-ray absorption and fluorescence effects can be neglected due to sufficient thinness of the FIB lamellae. Thus, the background subtracted raw elemental counts have only been modified by standardless Cliff-Lorimer k_{AB} factors that are incorporated in the EDAX software. However, it is generally accepted that only certain k_{AB} factors are sufficiently robust to use, and for this reason, we restricted the use of k_{AB} factors to Si, Al, K, and Ca for deriving their semiquantitative concentrations. On the other hand, the k_{AB} factor for O, for example, is not accurate and should be avoided. This is the reason why elemental atomic ratios are reported in this study (K/Si, Al/Si, Ca/Si), rather than complete chemical compositions. In general, quantitative chemical compositions based on STEM-EDX are only possible if external standards are analyzed, or alternatively, if an iterative ζ (zeta) method is used (Watanabe and Williams, 2006; Williams and Carter, 2009).

Supplemental Information 6

With respect to chemical mapping by EFTEM, as well as high resolution TEM images, the sharpness of a chemical or structural interface depends in large part on the orientation of the interface- in this study, this pertains specifically to the interface between the primary feldspar grains and the secondary precipitates. It cannot *a priori* be assumed that the interface will be planar and parallel to the vertical TEM electron beam. Thus, an irregular and/or oblique feldspar-precipitate interface will have a deleterious effect on the sharpness of a chemical or structural interface, or the accuracy of a spot analysis. Without going into too much detail, the interpretation of EFTEM chemical maps also requires caution, as thickness effects will affect the grey scale rendering of elemental concentrations. This is particularly important with respect to the amalgam of secondary precipitates, where significant thickness variations may exist.

As evidenced in the main text, in particular Fig. 11, chemical interfaces imaged in EFTEM chemical maps (jump ratio images) are far from sharp. Aside from arguments based on the orientation of the interface (see above), other factors also influence the sharpness, such the quality of the background fit to the EELS spectra, and the resolution of the post-column energy filter.

Table S1. Cation concentrations leached from hydrothermal products; element % conversions ($[\text{mass element } i]_{\text{leachate}} / [\text{mass element } i]_{\text{K-feldspar}}$) after contact with deionized water or 0.5 mol/L HCl

Sample	Phase	Concentration (ppm)			Conversion %			Concentration (ppm)			Conversion %			H ₂ O treatment/		
		H ₂ O treatment			H ₂ O treatment			HCl treatment			HCl treatment			HCl treatment (%)		
		Si	Al	K	Si	Al	K	Si	Al	K	Si	Al	K	Si	Al	K
FHS-1C	sanidine	0.57	0.06	5.06	0.93	0.30	29.26	36.87	16.55	9.86	59.98	79.27	57.04	1.55	0.37	51.29
SX-1C	microcline	1.19	0.07	8.92	1.94	0.34	37.37	37.73	15.14	14.86	61.39	77.18	62.25	3.15	0.44	60.02
LS-1C	microcline	2.08	0.02	7.91	3.39	0.09	36.98	39.10	16.58	12.94	63.82	81.77	60.48	5.31	0.11	61.14
LS-2C	microcline	2.39	0.02	9.18	3.93	0.08	41.35	39.50	16.35	13.61	65.06	79.29	61.32	6.04	0.10	67.43
WLST-1C	microcline	1.11	0.05	4.20	1.79	0.27	19.37	23.77	10.27	9.12	38.37	52.64	42.01	4.67	0.52	46.11
TYG-3C	microcline	1.19	0.03	4.75	1.92	0.16	25.47	33.12	13.95	11.68	53.36	71.13	62.60	3.60	0.22	40.69
TYG-4C	microcline	0.87	0.08	9.18	1.41	0.41	41.34	30.17	12.33	13.24	49.19	62.16	59.64	2.87	0.66	69.32

Table S2. FESEM-EDXS elemental concentrations (atom %) and ratios, with estimates for probable phases. XRF analyses of unaltered samples indicated for comparison. FESEM images not in main text: see Figs. S4-S10.

[illegible]

LS-1: area 8												
1	0	0	15.3	9.0	14.7	60.4	0	0.6	0	1.0	0.3	CASH
2	0	0	10.0	2.9	13.8	45.1	28.3	0.2	0	0.7	0.2	CASH + carb
XRF analysis	5.8	1.7	0	7.9	23.0	61.6	0	0.34	0.25	0	0	LS-1 unaltered
TYG-3: area 2												
1	1.9	1.3*	19.8	1.9	9.9	60.5	4.5	0.2	0.2	2.0	0.3	CASH + carb
2	0.2	0	17.2	11.5	6.3	64.0	0	1.8	0.02	2.7	0.3	CASH on microcline
3	1.3	0.8	15.3	1.5	8.8	39.3	32.4	0.2	0.14	1.7	0.4	CASH + carb
4	7.2	0	0	8.5	23.6	56.8	4.0	0.4	0.3	0	0	micro + resin (minor)
5	0.7	1.0*	19.6	5.3	10.9	48.4	14.0	0.5	0.07	1.8	0.4	CASH + carb
TYG-3: area 4												
1	1.0	1.7*	12.9	3.4	6.0	41.3	33.6	0.6	0.16	2.2	0.3	CASH + carb
2	0	0	15.7	10.2	6.4	67.7	0	1.6	0.0	2.4	0.2	CASH on microcline
3	1.8	0.8	26.3	1.3	12.6	51.8	5.2	0.1	0.14	2.1	0.5	CASH + carb
TYG-3: area 6												
1	1.4	1.7	19.1	2.6	11.1	50.8	12.5	0.2	0.12	1.7	0.4	CASH + carb
2	6.5	1.4	0.0	8.3	23.2	57.0	3.6	0.4	0.28	0.0	0.0	microcline
3	0.3	1.8*	12.2	5.2	9.2	59.6	10.8	0.6	0.04	1.3	0.2	CASH + carb
TYG-3: area 7												
1	0.9	2.7*	14.2	2.7	6.9	65.4	6.5	0.4	0.13	2.1	0.2	CASH + carb
2	0.5	0.0	25.8	7.2	8.5	58.1	0	0.8	0.06	3.0	0.4	CASH
3	0.3	0.0	15.7	9.4	7.7	65.8	0	1.2	0.04	2.0	0.2	CASH
4	1.1	2.7*	15.2	3.3	5.2	71.5	1.1	0.6	0.20	2.9	0.2	CASH + carb
5	0.3	0.0	17.6	7.9	10.4	63.6	0	0.8	0.02	1.7	0.3	CASH
6	0.5	0.0	14.1	6.6	7.6	57.6	13.6	0.9	0.06	1.9	0.2	CASH + carb
TYG-3C: area 9												
1	1.0	1.8*	19.0	4.7	8.4	62.4	2.3	0.6	0.11	2.3	0.3	CASH + carb (minor)
2	0.7	0.0	17.4	7.3	11.0	62.9	0	0.7	0.07	1.6	0.3	CASH
XRF analysis	5.0	2.5	0.1	7.6	23.2	61.6	0	0.33	0.22	0.00	0.00	TYG-3 unaltered
LS-2C powder area 11												
1	3.7	0.3	0.4	4.7	14.8	41.0	35.0	0.3	0.25	0.0	0.0	micro + resin
2	0.3	0.6	16.8	10.3	15.4	53.4	3.2	0.7	0.02	1.1	0.3	CASH + carb
3	0.2	0.6	12.9	7.3	12.1	61.1	5.8	0.6	0.02	1.1	0.2	CASH + carb
4	0.4	0.6	20.5	9.2	13.8	28.1	27.4	1.5	0.03	1.5	0.7	CASH + carb
5	0.4	0.2	7.7	0.4	2.3	29.7	59.3	0.2	0.17	3.3	0.3	CASH + carb
6	0.8	1.1*	5.1	1.3	5.0	34.7	52.0	0.3	0.16	1.0	0.15	CASH + carb
7	0.4	0.8*	6.2	3.6	6.9	41.1	41.0	0.5	0.06	0.9	0.15	CASH + carb
8	0.2	0.7*	10.7	6.8	12.4	59.8	9.5	0.5	0.02	0.9	0.2	CASH + carb
9	0.1	0.1	0.2	0.1	0.7	8.5	90.2	0.1	0.14	0.3	0.02	tape on sem stub
LS-2C area 1												
1	5.7	1.1	1.8	7.1	20.2	55.3	8.8	0.4	0.28	0.1	0.03	micro + carb (minor)
2	4.6	0.9	11.4	4.9	16.8	55.2	6.0	0.3	0.27	0.7	0.2	CASH + carb on micro
3	4.2	0.8	14.7	3.8	15.5	58.3	2.8	0.25	0.27	0.9	0.2	CASH + carb
4	3.7	1.1	17.1	3.4	14.6	57.9	2.3	0.23	0.25	1.2	0.3	CASH + carb
5	4.8	0.3	16.3	4.3	18.3	52.5	3.5	0.23	0.26	0.9	0.3	CASH + carb

LS-2C area 5												
1	0.9	1.2*	18.7	4.6	10.0	59.5	4.8	0.46	0.09	1.9	0.3	CASH + carb
2	2.3	0.6*	20.1	2.7	13.8	55.5	4.7	0.20	0.17	1.5	0.4	CASH + carb
3	0.5	0.0	14.8	6.9	10.7	65.5	0.7	0.65	0.05	1.4	0.2	CASH
4	2.4	0.7*	21.1	2.7	14.4	49.5	8.9	0.19	0.17	1.5	0.4	CASH + carb
LS-2C area 6												
1	1.6	2.1*	16.4	1.3	9.6	57.8	11.3	0.14	0.17	1.7	0.3	carb + CASH (minor)
XRF analysis	6.0	1.4	0.0	8.1	22.9	61.6	0	0.35	0.26	0.00	0.00	LS-2 unaltered
SX-1C area 3												
1	7.3	0.7	0.0	8.2	23.0	54.4	6.2	0.36	0.31	0.0	0.0	microcline
2	0.5	0.0	13.9	5.3	10.4	64.2	4.6	0.51	0.04	1.34	0.22	CASH + carb
3	3.0	0.0	34.7	1.1	13.8	47.4	0.0	0.08	0.22	2.51	0.73	CASH on microcline
4	0.3	0.0	15.4	6.6	10.6	61.8	3.9	0.63	0.03	1.46	0.25	CASH + carb
SX-1C area 4												
1	2.0	0.0	26.6	6.0	15.2	47.5	2.5	0.4	0.13	1.8	0.6	CASH + carb
2	14.7	0.0	40.5	1.0	16.8	25.4	1.5	0.06	0.88	2.4	1.6	CASH + carb
3	5.6	0.0	34.2	1.3	15.0	39.9	3.8	0.08	0.37	2.3	0.9	CASH + carb
XRF analysis	6.5	0.9	0.0	7.7	23.2	61.7	0	0.33	0.28	0.00	0.00	SX-1 unaltered
WLST-1C (GFZ 10-2018)												
1	6.9	0.5	0.0	7.7	24.0	56.5	4.4	0.32	0.29	0.0	0.0	microcline + minor precips
2	0.1	0	10.7	5.0	8.1	57.3	18.8	0.62	0.01	1.31	0.19	CASH + carb
3	3.2	0.6	3.7	3.9	13.7	50.1	24.9	0.28	0.24	0.27	0.07	CASH + minor carb
4	6.8	0.3	0.0	7.4	23.2	55.3	7.1	0.32	0.29	0.0	0.0	microcline + minor precips
5	1.1	0.3	11.3	0.8	5.4	33.8	47.3	0.15	0.21	2.10	0.33	CASH + carb
6	6.7	0.5	0.0	7.6	23.5	56.8	5.0	0.32	0.28	0.0	0.0	microcline + minor precips
XRF analysis	5.9	1.5	0.0	7.6	23.3	61.7	0	0.33	0.25	0.0	0.0	WLST-1 unaltered

sample & spot no.	K	Na	Ca	Al	Si	O	C	Al/Si	K/Si	Ca/Si	Ca/O	
FHS-1C (GFZ 10-2018)												
1	4.5	2.6	0	7.8	23.3	57.4	4.4	0.33	0.19	0	0	sanidine + resin (minor)
2	4.2	2.7	0	7.7	22.9	58.1	4.4	0.33	0.18	0	0	sanidine + resin (minor)
3	4.2	2.4	0	7.4	21.8	55.9	8.3	0.34	0.19	0	0	sanidine + resin (minor)
4	5.9	1.7	1.3	7.4	24.5	31.1	28.2	0.30	0.24	0.05	0.04	CASH + carb on sanidine
5	0.7	0.5	14.4	1.5	8.8	43.0	31.1	0.17	0.08	1.64	0.34	CASH + carb
6	0.7	0.4	14.0	1.1	4.7	40.9	38.3	0.23	0.15	2.98	0.34	CASH + carb
7	0.6	0.3	10.6	1.2	6.5	28.2	52.6	0.18	0.10	1.63	0.38	CASH + carb
8	1.0	0.5	31.4	0.6	4.2	49.8	12.5	0.13	0.24	7.41	0.63	CASH + carb
XRF analyses	4.6	2.6	0.1	8.1	22.9	61.7	0	0.35	0.20	0.00	0	FHS-1 unaltered

notes: CASH also includes CSH phases; carb = Ca-carbonate; *[Na] too high due to poor EDX peak fit; micro = microcline

References

- Ciceri, D., Close, T.C., Barker, A.V., Allanore, A., 2019. Fertilizing properties of potassium feldspar altered hydrothermally. *Communications Soil Sci. Plant Anal.* 50, 482–491.
- Ciceri, D., de Oliveira, M., Allanore, A., 2017. Potassium fertilizer via hydrothermal alteration of K-feldspar ore. *Green Chemistry* 19, 5187–5202.
- Ciceri, D., Manning, D.A.C., Allanore, A., 2015. Historical and technical developments of potassium resources. *Science Total Environment* 502, 590–601.
- Cliff, G., Lorimer, G.W., 1975. The quantitative analysis of thin specimens. *J. Microscopy* 103, 203–207.
- Cuong, T.X., Ullah, H., Datta, A., Hanh, T. C., 2017. Effects of silicon-based fertilizer on growth, yield and nutrient uptake of rice in tropical zone of Vietnam. *Rice Science* 24, 283–290.
- Guntzer, F., Keller, C., Meunier, J.-D., 2012. Benefits of plant silicon for crops: a review. *Agronomy Sustainable Devel.* 32, 201–213.
- Komarneni, S., Breval, E., Miyake, M., Roy, R., 1987. Cation-exchange properties of (Al + Na)-substituted synthetic tobermorites. *Clays & Clay Minerals* 35, 385–390.
- Mostafa, N.Y., Shaltout, A.A., Omar, H., Abo-El-Enin, S.A., 2009. Hydrothermal synthesis and characterization of aluminium and sulfate substituted 1.1 nm tobermorites. *J. Alloys Compounds* 467, 332–337.
- Reinik, J., Heinmaa, I., Mikkola, J.-P., Kirso, U., 2007. Hydrothermal alkaline treatment of oil shale ash for synthesis of tobermorites. *Fuel* 86, 669–676.
- O'Hara, G.W., Boonkerd, N., Dilworth, M.J., 1988. Mineral constraints to nitrogen fixation. *Plant Soil* 108, 93–110.
- Sanz Scovino, J. I., Rowell, D.L., 1988. The use of feldspars as potassium fertilizers in the savannah of Colombia. *Nutrient Cycling Agroecosystems* 17, 71–83.
- Wang, Z.H., Ma, S.H., Zheng, S.L., Wang, X.H., 2017. Incorporation of Al and Na in hydrothermally synthesized tobermorite. *J. Am. Ceram. Soc.* 100, 792–799.
- Watanabe, M., Williams, D.B., 2006. The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new ζ -factor methods. *J. Microscopy* 221, 89–109.
- Williams, D. B., Carter, C.B., 2009. *Transmission Electron Microscopy Part 4: Spectrometry*, Springer.
- Yang, J., Tan, X.M., Ma, H.W., Zeng, C., Peng, H., 2015. Alkali-hydrothermal synthesis of acicular tobermorite using natural mineral K-feldspar powder. *Ferroelectrics* 481, 57–63.
- Youssef, H., Ibrahim, D., Komarneni, S., Mackenzie, K.J.D., 2010. Synthesis of 11 Å Al-substituted tobermorite from trachyte rock by hydrothermal treatment. *Ceramics International* 6, 203–209.
- Zhai, Y., Zeng, Q., Hellmann, R., Liu, S., Liu J., Nan, J., 2020. Reaction mechanism during hydrothermal alteration of K-feldspar under alkaline conditions and nanostructures of the produced tobermorite. *Acta Petrologica Sinica*, 36, 2834–2844 (in Chinese with English abstract). doi 10.18654/1000-0569/2020

Figures S1a-d

LS-1

LS-2

SX-1

TYG-3

Figures S1e-g

TYG-4

WLST-1

FHS-1

Fig. S1. Secondary electron SEM micrographs of the unaltered feldspar samples. All are microcline, except sample FHS-1 (sanidine). Micrographs obtained with an SEM Merlin instrument operating at 1.2 kV and beam current of 500 pA.

Figure S2A

a

b

C

Fig. S2A. a. Powder X-ray diffraction patterns of the 6 unaltered microcline feldspars. Reference microcline and albite ICDD files are shown at bottom. b. Rietveld fit of LS-1 diffraction pattern. c. Rietveld fit of WLST-1 diffraction pattern. In both *b*) and *c*), measured data given by red crosses, calculated pattern in green, and from top to bottom (red, black ticks): positions of allowed $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections of microcline and albite, respectively (albite is considered as an exsolved phase). The rose-colored pattern at the very bottom represents the residuals (difference between measured and calculated diffraction pattern).

Figure S2B

Fig. S2B. a. Powder X-ray diffraction patterns of the unaltered sanidine feldspar. Reference sanidine and albite ICDD files are shown at bottom. b. Rietveld fit of FHS-1 diffraction pattern. The measured data given by red crosses, calculated pattern in green, and from top to bottom (red, black ticks): positions of allowed $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections of microcline and albite, respectively (albite is considered as an exsolved phase). The rose-colored pattern at the very bottom represents the residuals (difference between measured and calculated diffraction pattern).

Figure S3

a

b

Figure S3

c

d

Figure S3

e

f

Figure S3

gg

Fig. S3. Fitted X-ray powder diffraction patterns and Rietveld fits of the altered hydrothermal products derived from the 6 microcline samples and 1 sanidine sample (FHS-1). 9 Å tobermorite is the same as clinotobermorite, the term used in the main text.

Figure S4: LS-1C polished grain mount

Figure S4: LS-1C polished grain mount

Fig. S4c1, c2. FESEM images, modified from Fig. 5a, b Zhai et al., 2020

Figure S5A: LS-2C powder

Figure S5A: LS-2C powder

Figure S5A: LS-2C powder

Fig. S5A a-g. SEM micrographs of spheroids imaged in powder sample LS-2C. Based on EDX analyses, this is a Ca-Al-silicate phase that corresponds in composition to hydrogrossular. Nonetheless, hydrogrossular minerals all crystallize in the cubic system, making these images even more interesting. These spheroids can be observed in all of the other altered microcline and sanidine samples, as well. Even though not shown here, there is evidence that these spheroids are hollow. Note the irregular and interlocking polygonal plates visible in panels *d* and *e*. In panel *g* one can notice numerous tiny hollow spheroids growing on the surface of a large spheroid. The fibrous crystals are most likely tobermorite, based on morphology.

Figure S5B: LS-2C polished grain mount

Figure S5B: LS-2C polished grain mount

Figure S6: SX-1C polished grain mount

Figure S7: TYG-3C polished grain mount

Figure S7: TYG-3C polished grain mount

Figure S7: TYG-3C polished grain mount

Fig. S7e. In what appears to be an amalgam of CASH, CSH and calcium carbonate crystals, one can note how individual crystals have started coalescing together to evolve into a solid, carapace-like surface covering. This type of surface coverage by secondary precipitates may be more or less impermeable on a local scale (this was also evidenced in other samples). This suggests that such coverings may impede the access of water to the underlying substrate, which here appears to be a primary microcline grain. On a long-term basis, this could inhibit dissolution of primary feldspar grains.

Figure S8: TYG-4C polished grain mount

closeups of above

Figure S8: TYG-4C polished grain mount

note: spots 9 & 10 are located in rectangle, panel a

Figure S8: TYG-4C polished grain mount

Figure S9: WLST-1C polished grain mount

Figure S9: WLST-1C polished grain mount

Figure S10: FHS-1C polished grain mount

Fig. S11a. STEM image showing sharp interface of sanidine (black arrows) with secondary phases. This image was taken slightly below Fig. 11d in the main text. Note that in STEM, the sanidine appears white, while in BF it appears dark (e.g., Fig. 11d, main text). In this image one can also note the presence of a thin linear band a few tens of nm in width (medium grey color) that abuts the sanidine interface. Two sets of EDXS analyses are shown, and are labeled ‘5600 image 3’ (2 analyses on left side of image) and ‘5600 image 2’ (4 analyses on right side). EDXS chemical analyses are reported in Table 4, main text. Note that the material in area 4 is an extraneous metallic contaminant.

Fig. S11b. STEM image of sanidine grain- the exact position of the sandine interface is not evident, as it is obscured by a white band that is likely attributable to Ga deposition during FIB preparation. The inset shows an enlarged view of precipitates and nano-particles at outer edge. Their origin is not clear- they may represent nanophases formed during chemical alteration, or alternatively, they may also be an artifact of sample preparation. EDXS chemical analyses are reported in Table 4, main text.

Figure S11: FHS-1C, FIB-prepared TEM foil

Fig. S11c. STEM image of sanidine grain showing sharp interface (black arrows) and EDXS analysis locations. EDXS chemical analyses are reported in Table 4, main text.

Table 1a. Average chemical compositions of unaltered microcline and sanidine (FHS-1) samples based on XRF analyses (mass %)

Sample ID	Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ [†]	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Chemical formula
LS-1 (#1)	Lingshou	65.02	0.06	18.95	0.05	0.00	0.02	0.07	2.45	12.82	0.01	0.20	Na _{0.22} K _{0.75} Al _{1.03} Si _{2.99} O ₈
LS-2 (#7)	Lingshou	63.93	0.09	19.18	0.05	0.00	0.06	0.13	2.02	13.08	0.01	0.46	Na _{0.18} K _{0.78} Ca _{0.01} Al _{1.05} Si _{2.97} O ₈
SX-1 (#10)	Xiong'ershan	64.93	0.10	18.30	0.78	0.00	0.07	0.05	1.37	14.20	0.01	0.36	Na _{0.12} K _{0.84} AlSi _{3.01} O ₈
TYG-3 (#5)	Taiyanggou	66.40	0.01	18.57	0.12	0.00	0.04	0.19	3.59	11.18	0.01	0.22	Na _{0.32} K _{0.65} Ca _{0.01} Al _{0.99} Si _{3.01} O ₈
TYG-4 (#8)	Taiyanggou	65.40	0.02	18.70	0.14	0.00	0.05	0.12	2.13	13.29	0.02	0.22	Na _{0.19} K _{0.78} Ca _{0.01} Al _{1.01} Si ₃ O ₈
WLST-1 (#13)	Weilasituo	65.97	0.01	18.28	0.04	0.00	0.02	0.01	2.22	13.07	0.01	0.08	Na _{0.20} K _{0.76} Al _{0.99} Si _{3.02} O ₈
FHS-1 (#12)	Fenghuo Mt.	64.80	0.16	19.47	0.23	0.00	0.04	0.18	3.85	10.30	0.01	0.24	Na _{0.34} K _{0.60} Ca _{0.01} Al _{1.05} Si _{2.97} O ₈

† total iron oxide;

LOI: loss on ignition

Table 1b. Elemental atomic ratios of unaltered microcline and sanidine (FHS-1)(XRF) + secondary phases

sample or phase	(Na+K)/Si	K/Si	Al/Si	Ca/Si
LS-1 (#1)	0.32	0.25	0.34	0.00
LS-2 (#7)	0.32	0.26	0.35	0.00
SX-1 (#10)	0.32	0.28	0.33	0.00
TYG-3 (#5)	0.32	0.22	0.33	0.00
TYG-4 (#8)	0.32	0.26	0.34	0.00
WLST-1 (#13)	0.32	0.25	0.33	0.00
FHS-1 (#12)	0.32	0.20	0.35	0.00
avg microcline	0.32	0.25	0.34	0.00
calcite*	na	na	na	na
tobermorite*	0	0	0 [†]	0.83
hibschite*	0	0	0.71-1.33	1.07-2.00
katoite*	0	0	≥ 1.33	≥ 2.00

*based on nominal mineral formula

na = not applicable since [Si] = 0

[†] Wang et al. (2016) report Al/Si = 0.05 to 0.30 for Al-tobermorite

Table 2. BET (N₂) specific surface areas of microcline and sanidine (FHS-1) samples

Sample ID	BET _{N2} (m ² /g) (unaltered)	BET _{N2} (m ² /g) (altered)
LS-1C (#1)	2.5	10.0
LS-2C (#7)	4.0	11.0
SX-1C (#10)	1.9	9.5
TYG-3C (#5)	1.7	10.1
TYG-4C (#8)	1.5	9.8
WLST-1C (#13)	1.3	10.4
FHS-1C (#12)	1.0	10.4