fresh nepheline. Microphenocrysts of green pyroxene, magnetite, and rare red-brown biotite also occur.

Chemical analyses of specimens from the ash-flows are given in Table I and confirm their phonolitic composition. The tuffs have lower $SiO_2$ and $Al_2O_3$ and correspondingly higher volatile contents than the average plateau phonolite. The high $H_2O+$ content of the phonolites may be correlated with the presence of abundant groundmass analcime. The occurrence of analcime and primary calcite in a phonolite from Tiati has been reported by Webb (1973).

Ash-flows that are strongly undersaturated have not been previously reported. Even within the 50 000 km³ estimated volume of plateau phonolite lavas in Kenya, ash-flows appear to be exceedingly rare. The apparent low viscosity of the phonolite flows and their morphological similarities to basaltic lavas have been commented upon by Lippard (1973b). In general, the plateau phonolite magma seems to have maintained sufficient fluidity during vesiculation and extrusion to remain coherent and un-fragmented.

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# Microchemical determination of FeO and of available oxygen in minerals

THE main weakness of most methods currently available for the determination of the state of oxidation ('ferrous iron' or 'available oxygen') of milligram quantities of minerals is that they involve the addition of reagents that are difficult to remove and interfere with other determinations on the same solution. The present method avoids

this complication, thereby conserving material, and is applicable to almost any mineral that can be dissolved in concentrated hydrochloric acid, hot or cold. It depends on the fact that iodine monochloride in 5 to 8 $N$ HCl is a powerful oxidizing agent, reduction of which leads to free iodine, which can then be extracted and determined photo-metrically. In previous work (Davis et al., 1965; Hey et al., 1969) the author has titra-ted the liberated iodine with $M/200$ iodate, but extraction and photometry has proved both more convenient and more accurate. It has been used successfully for the determination of FeO in childrenite and for the determination of $IO_3^-$ in schwartz-embergite.

Iodine monochloride is a little-known reagent. Though hydrolysed by water, it is soluble without decomposition in hydrochloric acid of adequate strength, in which it is probably largely present as the ion $ICl_2^-$; on heating in a closed vessel, these solutions undergo the reaction $3\ ICl_2^- \rightarrow I_2 + ICl_4^- + 2Cl^-$ to a slight extent, but this is completely reversed on cooling. Pure solutions are stable indefinitely, but traces of dust or other oxidizable impurities may be oxidized, slowly in the cold and more rapidly on heating, with liberation of free iodine.

*Reagents.* The only reagents used are iodine monochloride solution, carbon tetra-chloride, and a standard solution of hydrazine hydrochloride. The carbon tetra-chloride must be free from oxidizable impurities; doubtful batches can be purified by digestion at 50 to 60 °C in a closed vessel with $M/6$ iodine monochloride solution for several days.

Unless potassium is to be determined in the same portion, the iodine monochloride is conveniently prepared as an $M/6$ stock solution in 9 $N$ HCl by the reaction $2\ KI + KIO_3 + 6\ HCl \rightarrow 3\ H_2O + 3\ KCl + 3\ ICl$; if potassium is to be determined, the reagent must be prepared by passing chlorine into a suspension of iodine in 9 $N$ HCl; in either case the reaction should be arranged to leave a little free iodine. For use, the stock solution is diluted with 9 $N$ HCl and extracted with $CCl_4$ to ensure stoichiometric composition of the ICl.

If it is to be used for the analysis of a mineral that is soluble in HCl quickly in the cold, the diluted and extracted ICl solution can be used directly, but if heat will be necessary it must first be stabilized to destroy traces of oxidizable impurities. This is done by heating the solution in a glass-stoppered flask on the water-bath for several days; after cooling, any liberated iodine is extracted with $CCl_4$, and the operation repeated until a digestion yields no more than traces of iodine. The stabilized solution must be protected from dust, and should not be kept more than a few days.

Hydrazine hydrochloride solutions are stable in air; an approximately 0·15 $M$ stock solution is standardized against $KIO_3$, and is diluted 1:100 for use (note that one $N_2H_5Cl$ is equivalent to 4 FeO). KI has been found an unsatisfactory standard on this scale, because the very dilute solutions necessary are rapidly oxidized in air.

Because iodine is not quantitatively transferred to $CCl_4$ in a single extraction, constant-volume multiple extraction is necessary, but reproducible results are readily obtained. The solutions of iodine in $CCl_4$ are stable for at least 6 months in well-stoppered flasks, and Beer's Law is obeyed to an extinction of at least 1·2.

*Determinations of reducing power ('ferrous iron').* A sample of the material, not

exceeding 15 mg and expected to contain between 100 and 1500 $\mu$g FeO or its equivalent in other reductants, is weighed into a dry 5 or 10 ml glass-stoppered flask, and 4 ml of approximately $M/12$ iodine monochloride in 9 $N$ HCl is added. No special precautions are needed if the mineral will dissolve in 1 or 2 hours in the cold, but if heating is necessary stabilized ICl must be used, and the flask should have been cleaned by heating a little of the stock ICl solution in it for several hours on the water-bath and rinsing with diluted stabilized ICl. Highly resistant minerals can be treated in sealed tubes at temperatures up to 200 °C, if elements extractable from the tube by acid can be neglected.

When reaction is complete, the solution is decanted from any insolubles into a 25 ml separator (the flask being rinsed with 2·5 ml of water) and extracted with several small portions of carbon tetrachloride, shaking vigorously for 2 min each time. The combined extracts are bulked to 10, 20, or 50 ml, according to the amount of iodine present, and photometered at $\lambda$ 520 nm against $CCl_4$ and a reagent blank that has been similarly treated.

A calibration curve is prepared using standard hydrazine hydrochloride solutions treated similarly (no heating will be needed); portions of 0·5 to 2·5 g of diluted ($\approx$ 0·0015 M) hydrazine hydrochloride solution are weighed into stoppered weighing bottles; each portion is transferred to a 25 ml separator with 4 ml $M/12$ iodine monochloride and enough water to make the total bulk approximately 7·5 ml, and the mixture is extracted with several small portions of $CCl_4$. The number and approximate volumes of the $CCl_4$ extractants should be the same for standards and unknowns.

The hydrochloric acid layer after extraction may be used for almost any other determinations (Ge is readily extracted from 9 $N$ HCl by $CCl_4$, but at the acidity at which the extractions are made, 5 to 6 $N$, very little will be extracted; $As^{3+}$, also extractable, will have been oxidized in ICl solutions). The digestion flask should be washed out and any insolubles filtered off, weighed, and an appropriate correction made.

The method has proved very satisfactory for the determination of FeO in the difficultly soluble phosphates childrenite, oxychildrenite, and eosphorite; samples of 3 to 15 mg were employed, the FeO present ranging from 2 to 20 %. One sample of eosphorite from Itinga, Minas Gerais, Brazil (B.M. 1973, 59), was used for test analyses: five portions of the same well-mixed powder gave 11·9, 12·4, 11·6, 12·2, 12·2 % FeO (mean 12·1±0·2 %) by the present method, and 12·1, 12·1, 12·6, 12·7, 12·4, 12·9, 12·8 % by a dipyridyl method after solution in HF+$H_2SO_4$ (mean 12·5±0·2 %); all these determinations were made on portions of 10 to 20 mg.

*Determinations of oxidizing power* ('*available oxygen*'). This is carried out in exactly the same way as the determination of reducing power, except that, after the mineral has been dissolved in the ICl reagent, a known amount of a suitable reducing agent, expected to be a small excess, is added. This reduces the $ICl_4^-$ formed by oxidation of the ICl, and the excess reductant liberates some iodine, which is extracted and photometered (if the first extraction shows no iodine, a further small addition of reductant must be made). A blank experiment is carried through in parallel, using the same amounts of ICl reagent and reductant; the oxidizing power of the mineral is then

obtained by difference. Hydrazine hydrochloride will usually be found a convenient reductant $(N_2H_4 + O_2 \rightarrow N_2 + 2H_2O)$. The procedure was found very satisfactory for the determination of the $IO_3$ radical in schwartzembergite.

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# Domain structure in garronite: a hypothesis

GARRONITE, described as a new zeolite by Walker (1962), is similar to gismondine but was considered an independent species because of its higher symmetry and its higher Si-content. According to Fischer (1963), gismondine is monoclinic pseudo-tetragonal $P2_1/c$ with $a$ 10·02, $b$ 10·62, $c$ 9·84 Å, and $\beta = 92° 25'$, $b$ being the pseudo-quaternary axis; its framework is topologically tetragonal $I4_1/amd$. Gismondine has an ordered distribution of Si and Al in the tetrahedra. Since the ratio Si:Al is close to 1, the structure presents an alternation of $SiO_4$ and $AlO_4$ tetrahedra in accordance with the Loewenstein rule. This ordered distribution lowers the symmetry of the framework from the tetragonal to the monoclinic system.

The unit cell of garronite was shown by Barrer, Bultitude, and Kerr (1959) to be tetragonal by means of X-ray powder data ($a$ 10·01, $c$ 9·87 Å); Taylor and Roy (1964) found $a$ 9·85 and $c$ 10·32 Å. After Walker (1962), garronite is optically uniaxial at one end of the elongated crystals, but biaxial and twinned at the other.

Now one of us (A. A.) has obtained X-ray single crystal photographs of garronite, which contain only diffuse spots and hence are unsuitable for structure determination, but nevertheless confirm on the whole the tetragonal symmetry. We feel these data are now sufficient to put forward the following hypothesis: garronite crystals grow as single crystals with a disordered gismondine framework, but subsequently undergo a partial disorder–order transformation with formation of submicroscopic domains of four kinds. The possibility of four kinds of domains arises from the fact that in the disordered tetragonal form we have $a = b$ and $\gamma = 90°$, whereas in the ordered mono-clinic form $a \neq b$ and $\gamma \neq 90°$: in each zone of the disordered crystal, when ordering starts, we may have $a > b$ or $a < b$, and also $\gamma > 90°$ or $\gamma < 90°$.